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ABSOLUTE RATE OF THE REACTION OF BROMINE ATOMS WITH OZONE FROM 200 - 360 K

by

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ABSTRACT

The rate constant for the reaction $Br + O_3 \rightarrow BrO + O_2$ has been measured from 200 - 360 K by the technique of flash photolysis coupled to time resolved detection of bromine atoms by resonance fluorescence (FP-RF). Br atoms were produced by the flash photolysis of CH_3Br at $\lambda > 165$ nm. $[O_3]$ was monitored continuously under reaction conditions by absorption at 253.7 nm. At each of five temperatures the results were independent of substantial variations in $[O_3]$, total pressure (Ar), and limited variations in flash intensity (i.e. initial [Br]). The measured rate constants obey the Arrhenius expression, $k = (7.74 \pm 0.50) \times 10^{-12} \exp(-603 \pm 16/T)$ cm^3 molecule^{-1} s^{-1}, where the error quoted is two standard deviations. The results are compared with previous determinations which have employed the discharge flow-mass spectrometric technique.

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INTRODUCTION

The concern over the possible modification of the earth's stratospheric ozone layer from man made sources has prompted considerable research into the detailed understanding of stratospheric chemistry.[1] The controversy surrounding Cℓ atom release is well known.[1,2]

Concern regarding tropospheric bromine release with subsequent stratospheric effects has also been expressed.[3] The major release is apparently from the natural source, marine aerosols, but there is also substantial release from the agricultral use of CH_3Br as a fumigant, from the combustion products from leaded gasoline, and, to a lesser extent, from the use of CF_3Br as a fire suppressant. Other man made sources may also be documented in the future.

If bromine atoms are produced in the stratosphere from these sources, they would undoubtedly undergo transformations similar to Cℓ

$$Br + O_3 \rightarrow BrO + O_2 \qquad (1)$$

$$O + BrO \rightarrow Br + O_2 \qquad (2)$$

thereby catalyzing the chain destruction of ozone. Since the "sink" reactions of Br with most hydrogenous stratospheric species are negligible (unlike the Cℓ atom case), the potential destruction effects may be considerable depending on (a) absolute [Br] in the stratosphere and (b) the rate constants for odd bromine species including reactions (1) and (2).[3]

These factors have motivated the present study of the rate constant for reaction (1). Two previous determinations have been reported,

one being at room temperature only[4] and the other extending to the mid-stratospheric temperature of 224 K.[5] Both determinations were made in discharge flow systems with mass spectrometric detection of O_3. By way of contrast, the present study employed flash photolysis techniques with detection of Br via resonance fluorescence. The rate constant was measured at five temperatures from 200 - 360 K, and therefore, the stratospheric temperature regime is well overlapped.

EXPERIMENTAL

The technique employed in the present study is flash photolysis-resonance fluorescence (FP-RF). The apparatus and general techniques have been described previously;[6,7] however, in the present study, significantly more detail will be given since this work represents the first study of Br atom reactions by the FP-RF technique.

Br atoms were produced by the flash photolysis of CH_3Br at $\lambda > 165$ nm (suprasil cut off).[8] Bromine atom resonance radiation was obtained from a flowing pre-mixed Br_2-He mixture ($X_{Br_2} = 0.0002$) through the microwave discharge lamp at 0.3 torr. The reasonantly scattered photons at $145 < \lambda < 163$nm[9] were observed at right angles through sapphire windows ($\lambda \geq 145$ nm) and flowing dry N_2 in front of the photomultiplier. Preliminary photolysis experiments at flash energies greater than 60 J with only CH_3Br - Ar mixtures showed substantial initial non-linearity in first order plots when larger mole fractions of Br_2($X_{Br_2} = 0.001$) were used in the resonance lamp. This behavior generally indicates either too high an optical depth in the reaction cell (i.e. [Br] is not proportional to counts) and/or substantial reversal in the resonance source. Since the effect could be eliminated by decreasing the Br_2 mole fraction to 0.0002 and no flash energy dependence was noted in the strictly linear first order plots, the initial non-linearity had to be due to substantial reversal in the source. The lamp output with $X_{Br_2} = 0.0002$ was additionally observed with a McPherson 218 vacuum monochromator, and the multiplet intensities were similar to those reported previously for a pure Doppler source[9] but did indicate some self reversal. From the quality of the first order plots, the invariance of decay constants over a large change of flash energy (i.e., $[Br]_o$), and the multiplet structure, we conclude that the fluorescent signal is linearly proportional to [Br].

Ozone was generated by an electrical discharge in 120 torr O_2 and was collected on silica gel at 77 K.[10] Preliminary experiments were performed to test whether this fairly reactive compound would have long term stability in the experimental apparatus. The vacuum line was modified to accommodate a 154.5 cm path length photometer section with a low pressure mercury lamp and a 254 nm interference filter serving as the source of 253.7 nm light and a 1P28 photomultiplier serving as the detctor. The absorption coefficient of O_3 is known with high accuracy at this wavelength[11] (308.5 cm^{-1} atm^{-1}, base e and 273 K). With the pressure measuring devices on the system we were able to reproduce the well known coefficient within 5%. This showed that the procedures used for ozone purification were quite adequate and that the compound was stable in the system.

Since analyses of ternary O_3 - CH_3Br - Ar mixtures were anticipated, a determination of the absorption coefficient for CH_3Br was performed ($k_{CH_3Br,\ 253.7\ nm}$ = (0.134 $\pm$ 0.003) cm^{-1} atm^{-1}, base e and 298 K) which showed that negligible corrections were necessary for the ternary mixtures.

Ozone in the ternary mixture was then photometrically analyzed for long term stability. No change in $[O_3]$ was observed for the experimental mixtures of the present study over a time period of four hours; however, a loss of $\sim$ 15% was noted after 24 hours. This necessitated making new mixtures daily.

Finally it was necessary to establish that ozone was not lost by passage through the brass reaction vessel with stainless inlet and outlet ports. Initial levels of ozone in mixtures were measured photometrically before passing through the reaction vessel. Then photometric analysis of the exit mixture was performed at the temperatures of the present study as a function of flow rate through the system. If the flow rates were maintained at high enough levels, no appreciable loss was observed for all of the temperatures studied. An attempt was made to measure the rate constant at 400 K, but the loss rate was appreciable even under the fastest flow rate conditions available with the equipment. Generally the necessary flow rates were higher than in all previous studies from this laboratory so the contents of the cell were replenished several times between successive flashes.

Argon (Matheson, 99.9995%) and helium (Airco, 99.9999%) were used without further purification. Bromine (Fisher Scientific, 99.95%) was bulb to bulb distilled at 240 K, and the middle third was retained. Methyl bromide (Matheson, 99.5%) was similarly purified at 183 K. Ozone was synthesized daily and was collected on silica gel at 77 K. The sample was thoroughly outgassed at 250 K before usage.

RESULTS

Under the pseudo-first-order conditions employed here with $[O_3] >> [Br]$, the decay of Br atoms may be represented by

$$\ell n[Br] = - k_{observed}\, t + \ell n[Br]_o \qquad (3)$$

and $k_{observed}$ is given by

$$k_{observed} = k_1[O_3] + k_d \qquad (4)$$

k_1 is the reaction rate constant for reaction 1 and k_d is the decay constant due to diffusional loss. The pseudo-first-order decay constant, $k_{observed}$, was obtained by linear least squares methods from the exponential decay of bromine atom resonance fluorescence with $[Br] << [O_3]$. A consideration of the known oscillator strengths of the multiplets and the behavior of this system relative to that of other atomic systems suggests that $[Br]_o \leq 5 \times 10^{11}$ cm^{-3}. Thus, the condition for isolation of reaction by the usual first order analysis is well established if secondary reactions can be eliminated. The decay constant, however, is composite and contains contributions from both reaction and diffusion of atoms out of the reaction zone. k_d was obtained in separate experiments with only added CH_3Br under identical conditions as in the reactant experiments. The rate constant for Br + CH_3Br[12] is negligibly slow under the present conditions so the decay clearly refers to diffusional loss alone.

Typical first order plots are shown in Figure 1 where it is seen that the diffusional correction term is small. For all of the results presented here, this correction term never exceeds 10% of the decay when ozone is present.

Experiments were performed as a function of flash energy, and a strong intensity effect was noted at higher flash energies. Some typical results for T = 360 K are shown in Figure 2 where $\log_{10}$ (counts/flash) are plotted vs time at the four flash energies indicated on the left hand ordinate. Note that the initial counts/flash ($[Br]_o$) scales linearly with flash energy which is further quantitative experimental evidence that counts/flash is directly proportional to [Br] over the entire range. Even so, a strong non-linearity in the decay is noted particularly at 144 J. The non-linearity is evident even in the lower flash energy experiments. This behavior indicates that secondary processes occur which evidently re-form bromine atoms at long reaction times. The effect can be ascribed to reactive initial photolysis products and/or to secondary products produced by reaction 1. Because the flash lamp is broad band, ozone is undoubtedly photolyzed producing oxygen atoms in substantial quantities. The rate constants of O atoms with O_3[13] and CH_3Br[14] indicate that O atom depletion will be rather slow for the $[O_3]$ and $[CH_3Br]$ used here. Because [O] can be therefore substantial, we believe that this re-formation of bromine atoms is due to the reaction between the initially formed O atoms and the secondary radical, BrO. The rate constant for reaction 2 is large and has been estimated at $k_2 \simeq 1.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.[15] Unfortunately unambiguous measurement of $[O(^3P)]$ with the low wavelength cutoff limited by CaF_2 is not possible since the observed fluorescent signal would arise from both O and Br atomic scattering. Quantitative evaluation from absolute count rates would then require an accurate knowledge of photomultiplier sensitivities and window transmittances at the resonance lines for both O and Br atoms. In any case the effect could be eliminated by using low flash energies and limiting the length of time over which the decay constant is calculated. This is illustrated in Figure 2 where invariance in the decay constant within experimental error is seen in the three lower flash energy experiments if the initial decays are taken over the indicated time.

This re-formation of bromine atoms is even more severe at T = 200 K as shown in Figure 3 and is consistent with the occurrence of reaction 2 since this reaction likely has less temperature dependence than the initiating reaction 1. Nevertheless, the decay constants are invariant in the initial stages, and the isolation of the decay due only to reaction 1 is evident.

Thus, k_1 was calculated from $k_{observed}$ according to equation 4 from the known $[O_3]$. Experiments at each temperature were performed with substantial changes in total pressure and $[O_3]$ and limited changes in flash intensity and the results are given in Table I.

Figure 4 shows an Arrhenius plot of the mean k_1 values obtained at five temperatures. A linear least squares treatment yields the equation, $k_1 = (7.74 \pm 0.50) \times 10^{-12} \exp(-603 \pm 16/T)$ $cm^3 molecule^{-1} s^{-1}$. The indicated errors are increased to two standard deviations to account for possible systematic errors in the use of limited time intervals in first order decay constant analysis.

DISCUSSION

The present results are compared to the two previous studies in Table II. Clyne and Watson[4] have combined a discharge flow reactor with mass spectrometric detection. k_1 was measured under pseudo-first-order conditions with $[Br] >> [O_3]$. They obtained a room temperature value of $(1.2 \pm 0.2) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. The only previous variable temperature study is that of Leu and DeMore[5] who also used a discharge flow reactor coupled to mass spectrometric detection again with $[Br] >> [O_3]$. They obtain $k_1 = (3.34 \pm 0.40) \times 10^{-11} \exp(-978 \pm 32/T)$ cm^3 molecule^{-1} s^{-1}. This result is compared to the present result, $k_1 = (7.74 \pm 0.50) \times 10^{-12} \exp(-603 \pm 16/T)$ cm^3 molecule^{-1} s^{-1}, in Figure 4.

Inspection of the results of the three studies shows good agreement at room temperature, the variations being well within combined experimental errors. The present result and that of Leu and DeMore at 257 K are exactly the same, and at 233 K, are in agreement within combined experimental errors. However, the present result at 360 K appears to be lower by about 35% to that of Leu and DeMore. Nevertheless, the rate constant is well characterized under stratospheric temperature conditions (200-260 K), the greatest discrepancy amounting to $\pm$ 20%. In view of the limiations imposed by the re-formation of Br in the present FP-RF study and the rather severe axial gradient of [Br] in the discharge flow experiments (6-26% wall loss for $238 \leq T \leq 274$K), the discrepancy of $\leq \pm$ 20% for $200 \leq T \leq 260$ K is quite acceptable.

We note that the present result will not change the principal conclusions of Wofsy, et al.[3] regarding the potential modification of

the stratospheric ozone layer by atmospheric bromine release. The rate constant value used for k_1 in their model calculation is similar to that obtained here over the stratospheric temperature range. They have considered two termination reactions

$$Br + HO_2 \rightarrow HBr + O_2 \tag{5}$$

$$Br + H_2O_2 \rightarrow HBr + HO_2 \tag{6}$$

With the source strength suggested by Wofsy, et al.,[3] reaction 5 will likely be the only important "sink" reaction for Br in the stratosphere. A recent determination of the rate constant for Cℓ atoms with H_2O_2[16] where $\Delta H^o_{298} = -13.7$ kcal mole^{-1} suggests that reaction 6 ($\Delta H^o_{298} = 2.0$ kcal mole^{-1}) is totally negligible at estimated H_2O_2 concentrations in the stratosphere. Thus, the sensitivity of model predictions to reaction 5 will be even greater in this case than in the analogous reaction with Cℓ atoms.

Finally, though the reported rate constants are in adequate agreement with those of Leu and DeMore[5] from 200-298 K, the higher temperature values do not agree, and this is reflected in rather different Arrhenius parameters (Table II). Because these quantities have theoretical significance to chemical kinetics, additional experiments with the discharge flow-resonance fluorescence technique are currently in progress in this laboratory.[17]

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17. J. V. Michael and W. A. Payne. The experiments yield (5.4±0.3) $\times 10^{-13}$, (7.4±0.4)$\times 10^{-13}$, (11.2±0.7)$\times 10^{-13}$, and (14.4±1.0)$\times 10^{-13}$ all in units of cm^3 $molecule^{-1}$ sec^{-1} at 233.5 K, 257 K, 298 K, and 360 K respectively, in close agreement with the present results.

TABLE I. Rate Data for the Reaction Br + O_3

T / K	O_3 / mTorr	CH_3Br / mTorr	Ar / Torr	F.E.[a] / J	No. of Expts.	k_1 [c] / 10^{-13} cm^3 $molecule^{-1}$ sec^{-1}
200	89.3	50.4	60	20-68	3	3.57 ± 0.16
	67.0	37.8	45	36, 63	2	2.83 ± 0.18
	45.2	25.2	60	56	1	3.98
	45.2	25.2	30	63, 81	2	4.05 ± 0.21
	22.6	12.6	15	56, 81	2	4.97 ± 0.23
					10	3.84 ± 0.75[d]
225	59.5	45.0	60	36, 56	2	4.82 ± 0.50
	43.2	60.0	60	110,144	2	5.58 ± 0.05
	40.2	30.0	40	38, 46	2	5.30 ± 1.46
	29.3	40.0	40	110, 144	2	4.98 ± 1.03
	26.9	48.0	40	81, 144	2	5.36 ± 0.12
	20.3	15.0	40	56	1	5.98
	20.0	15.0	20	46, 56	2	5.58 ± 0.31
	14.6	20.0	40	36, 144	2	5.67 ± 0.18
	14.2	20.0	20	110, 144	2	4.41 ± 0.23
	9.9	7.5	20	56	1	5.34
	7.1	10.0	20	36, 56	2	5.07 ± 0.44
					20	5.24 ± 0.61[d]
257	38.8	77.8	70	81, 144	2	7.49 ± 0.35
	25.3	50.0	45	55-163	4	7.41 ± 0.12
	11.0	22.2	20	144	1	7.77
					7	7.48 ± 0.21[d]
298	43.0	101.0	70	56-144	4	9.09 ± 0.42
	41.4	43.8	70	95, 163	2	9.81 ± 0.89
	28.9	59.1	45	36-95	4	10.3 ± 0.36
	27.8	65.0	45	56-144	4	9.93 ± 0.83
	26.6	28.1	45	56-144	4	10.9 ± 1.05
	12.8	26.3	20	56-144	5	10.9 ± 0.78
	11.7	28.9	20	56-144	6	9.83 ± 0.80
					29	10.13 ± 0.91[d]
360	48.9	64.4	60	18-81	5	15.6 ± 0.73
	36.3	48.3	45	20-95	3	15.4 ± 0.79
	28.5	60.0	60	14-56	5	14.2 ± 2.18
	23.2	32.2	30	28-95	3	14.1 ± 0.68
	18.6	40.0	40	14-56	4	14.0 ± 1.23
	14.4	30.0	60	56	2	13.1 ± 0.35
	11.0	16.1	15	38, 95	2	15.6 ± 0.62
	9.2	20.0	40	56	2	14.1 ± 0.66
	8.9	20.0	20	20-56	3	14.9 ± 1.54
	4.4	10.0	20	56	2	15.3 ± 1.62
					31	14.63 ± 1.39[d]

a. Suprasil filter on flash lamp except where noted.
b. Sapphire filter on flash lamp.
c. Error limit is the standard deviation.
d. Mean value at that temperature.

TABLE II. Comparison of Rate Data for the Reaction Br + O_3

k at 298 K 10^{-12} molecule^{-1}sec^{-1}	A cm^3 molecule^{-1} sec^{-1}	E cal mole^{-1}	T/K	Technique[b]
1.2 ± 0.2	--	--	298	DF-MS/Clyne and Watson
1.16 ± 0.16	(3.34 ± 0.40)x10^{-11}	1943 ± 68	224-424	DF-MS/Leu and DeMore[5]
1.01 ± 0.18[a]	(7.74 ± 0.50)x10^{-12}[a]	1198 ± 32[a]	200-360	FP-RF/This Study

a. Error limits are two standard deviations.

b. DF-MS: Discharge flow-mass spectrometry; FP-RF: Flash photolysis-resonance fluorescence.

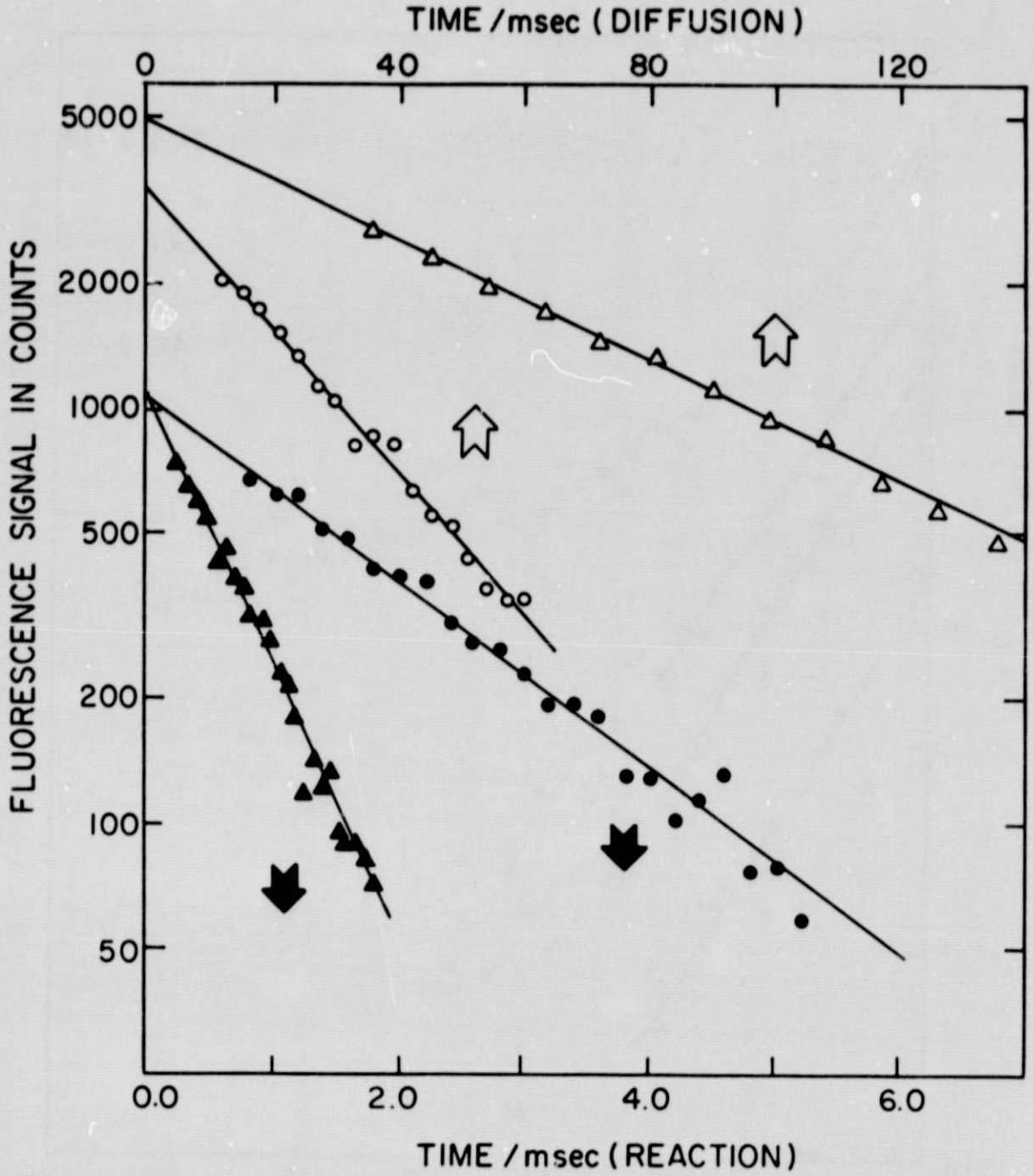
FIGURE CAPTIONS

Fig. 1: Typical plots of log (counts) (i.e. log [Br]) vs time illustrating decays of signal under reactant (with $[O_3]$) and diffusion ($[O_3] = 0$) conditions. Diffusion experiments are the open symbols and refer to the upper abscissa. Reactant experiments are the closed symbols and refer to the lower abscissa. Δ - T = 360 K, P_T = 45 torr, flash energy = 36 J, and P_{CH_3Br} = 56.3 mtorr. O - T = 360 K, P_T = 15 torr, flash energy = 95 J, and P_{CH_3Br} = 18.8 mtorr. ▲ - T = 360 K, P_T = 45 torr, flash energy = 46 J, P_{CH_3Br} = 48.3 mtorr, and P_{O_3} = 36.3 mtorr. ● - T = 360 K, P_T = 15 torr, flash energy = 95 J, P_{CH_3Br} = 16.1 mtorr, and P_{O_3} = 11.0 mtorr.

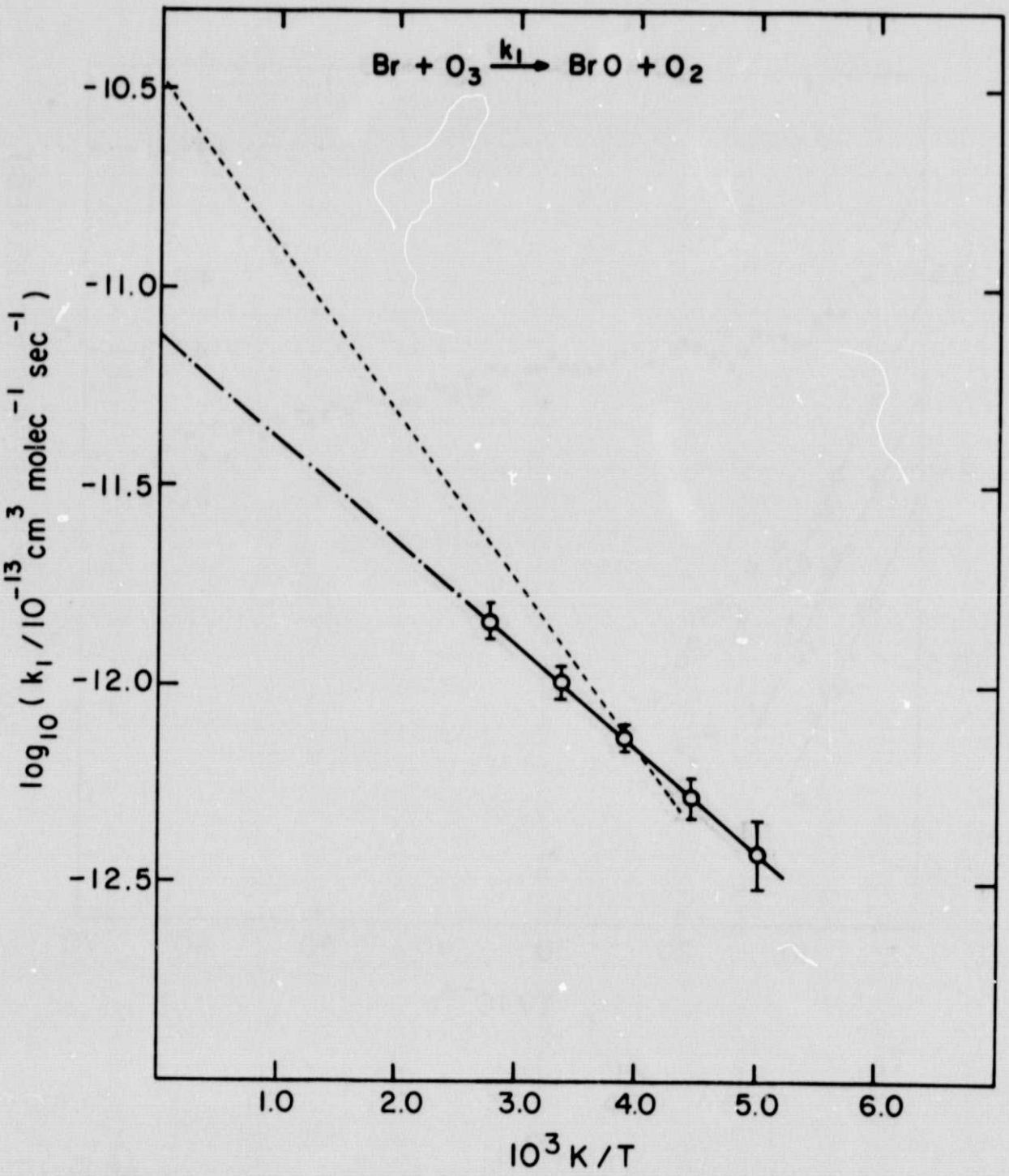
Fig. 2: Normalized decay plots (log (counts/flash) vs t) at four flash energies showing the long time re-formation of Br atoms. The right hand ordinate refers to flash energy and shows the correlation with $[Br]_o$. The solid lines are linear least squares lines over the indicated time interval. The dotted line is an extrapolation from the first point to t = 0 on the basis of the average of the three decay constants shown. T = 360 K, P_T = 60 torr, P_{CH_3Br} = 64.4 mtorr, and P_{O_3} = 48.9 mtorr.

Fig. 3: Normalized decay plot at T = 200 K. See caption to Fig. 2. P_T = 60 torr, P_{CH_3Br} = 50.4 mtorr, and P_{O_3} = 89.3 mtorr.

Fig. 4: Arrhenius plot for $Br + O_3 \rightarrow BrO + O_2$. O - present results with error bars of one standard deviation. The solid line is evaluated by linear least squares analysis. The dotted line is from reference 5.



1.5
1.0
0.5
0
-0.5
-1.0
5
10
15
20
25
30
35
144 J
81 J
46 J
18 J
log10 (COUNTS/FLASH)
log10(0.19 · FLASH ENERGY/ JOULES)
t / 10^-4 s


Br + O3 k1 → BrO + O2
-10.5
-11.0
-11.5
-12.0
-12.5
log10 (k1 / 10-13 cm3 molec-1 sec-1)
1.0
2.0
3.0
4.0
5.0
6.0
10^3 K / T

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15. Supplementary Notes

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